

In Search of Alternative Propellants for Ion Thrusters

*Presented at Joint Conference of 30th International Symposium on Space Technology and Science,
34th International Electric Propulsion Conference and 6th Nano-satellite Symposium
Hyogo-Kobe, Japan
July 4–10, 2015*

Kristof Holste*, Waldemar Gärtner†, Peter Köhler‡, Patrick Dietz§, Jennifer Konrad¶,
Stefan Schippers||, Peter J. Klar,** Alfred Müller,†† Peter R. Schreiner‡‡
Justus-Liebig-University Giessen, 35392, Germany

Abstract: We present a comparative overview about properties of materials suitable for electric propulsion. Furthermore, new types of materials that fulfill most of the recommended properties will be introduced as a potential alternative propellant. A newly built experimental setup facilitating the performance analysis of these materials will be presented.

Nomenclature

FEEP	= field-emission-electric-propulsion
GIT	= gridded ion thruster
HET	= Hall-effect thruster
I_i	= ionization potential
Isp	= specific impulse
M	= atomic mass
PPT	= pulsed plasma thruster
RIT	= radiofrequency ion thruster
T_b	= boiling temperature
v_{ex}	= exhaust velocity

*Research Associate, Institute of Experimental Physics I, Kristof.Holste@exp1.physik.uni-giessen.de

†PhD Student, Institute of Experimental Physics I, Waldemar.Gaertner@physik.uni-giessen.de

‡PhD Student, Institute of Experimental Physics I, Peter.E.Koehler@physik.uni-giessen.de

§Master Student, Institute of Experimental Physics I, Patrick.Dietz@physik.uni-giessen.de

¶Bachelor Student, Institute of Experimental Physics I, Jennifer.Konrad@materialwiss.uni-giessen.de

||Adjunct Professor, Institute of Experimental Physics I, Stefan.E.Schippers@physik.uni-giessen.de

**Professor, Institute of Experimental Physics I, Peter.J.Klar@exp1.physik.uni-giessen.de

††Professor emeritus, Institute of Atomic and Molecular Physics, Alfred.Mueller@iamp.physik.uni-giessen.de

‡‡Professor, Institute of Organic Chemistry, prs@org.chemie.uni-giessen.de

I. Introduction

THE ionization of a propellant and the subsequent acceleration of the propellant's ions is the fundamental principle behind generating thrust with an ion thruster. Besides the technical aspects of an ion thruster, the choice of an appropriate propellant is mandatory for efficient operation of the device with respect to the consumption of energy, fuel, and the total lifetime of the thruster as well as the whole satellite if one regards the interaction between ions and satellite surfaces. The following text will provide an overview about materials that are suitable as propellants for electric propulsion, and stress the advantages and disadvantages of these materials. The text focuses on gridded ion thrusters (GIT) and Hall-effect-thrusters (HET), other concepts like Field-Emission-Electric-Propulsion (FEED) and Pulsed Plasma Thrusters (PPT), and crystal ion emitters will not be discussed.

Ion thrusters like GIT and HET perform the ionization of propellants by electron-impact ionization in a delimited plasma volume, from which ions can be extracted and accelerated via electric fields, e.g., by an extraction grid system. The ionized material has to fulfill various requirements to be considered as a propellant. These properties will be discussed in detail in section II. Furthermore, a group of materials will be presented, which seems to have interesting properties for the usage as a propellant for ion thrusters. An experimental setup for testing these materials as well as first experimental results with new propellants will be given in section III.

II. Ion thruster propellants

A. General demand

The main mechanism for the ionization of the propellant is electron-impact ionization. The efficiency of this process depends on the cross-section of the ionization. A low ionization threshold may be promising for a material to be considered as a propellant, but this condition alone is not sufficient for motivating such a choice, since a high ionization cross-section is desirable as well. A convenient propellant combines low threshold and high cross-section values so that a certain amount of available energy for the ionization is used as efficiently as possible. For space applications this is an important aspect due to the limitation of energy reserves.

For thrust production the propellant mass does not play a role because the thrust transfer is performed by mass-independent electrostatic forces between the ion charge and the extraction grid system. Nevertheless, high propellant masses are mandatory to reduce the required power-to-thrust ratio or, equivalent, to reduce the required amount of propellant, which has to be ionized. Assuming a thrust of 1 mN and an ion energy of 1.5 keV, protons expelled by a thruster would require at least 0.269 kW mN^{-1} , whereas a beam of singly charged xenon ions would consume 0.235 kW mN^{-1} , which corresponds to a reduction of required beam power by about 12%. Starting from the same extracted beam current, e.g., 170 mA, and same ion energy of 1.5 keV, the number of extracted particles per time unit has to be the same, in our case $dN/dt = 1.06 \times 10^{18} \text{ s}^{-1}$. The extracted ions mass per time unit is $dM/dt = 1.78 \times 10^{-9} \text{ kg s}^{-1}$ and $2.31 \times 10^{-7} \text{ kg s}^{-1}$ for protons and xenon, respectively. With the different exhaust velocities for protons ($v_{ex} = 5.36 \times 10^5 \text{ m s}^{-1}$) and xenon ($v_{ex} = 0.47 \times 10^5 \text{ m s}^{-1}$), one can calculate the equivalent thrust with $dM/dt \cdot v_{ex}$, which reveals the same increase of thrust performance. Hence, the mass does not play a role in the production of thrust, but it plays an important role in terms of thrust efficiency.

From another point of view the non-gaseous propellants have to be brought into the gas phase without complex technical efforts, therefore, high boiling points should be avoided. For molecular propellants the fragmentation of the molecule has to be taken into account. Propellants of a high molecular mass will produce thrust ineffectively, if the molecule dissociates into lighter fragments. Another important aspect is the high availability of the propellant, which results in a low price and makes these types of ion engines economically attractive. The following sections discuss various atomic and molecular materials suitable for electric propulsion and introduces a promising candidate as an alternative propellant.

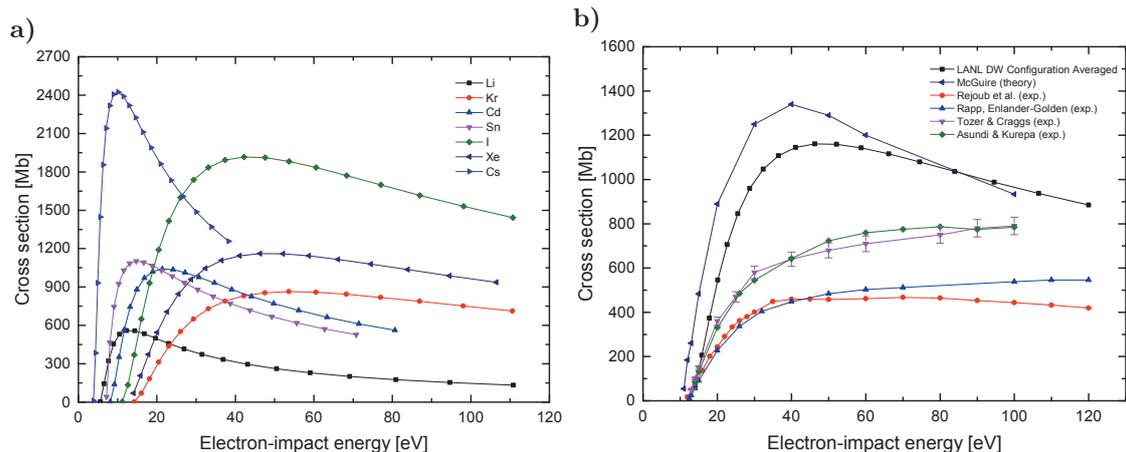


Figure 1. a) Theoretical ionization cross-sections for the materials given in Table 1. The computations have been done with the online version of the Los Alamos National Laboratory Atomic Physics Code (LANL, available at <http://aphysics2.lanl.gov/cgi-bin/ION/runlanl08d.pl>) using a configuration average of the final ionic states. The cross sections show different shapes with respect to threshold and absolute values, therefore, comparison of propellants only by the ionization potential is not sufficient. b) Comparison of the theoretical electron-impact ionization cross-sections of neutral xenon obtained from the LANL code and McGuire with experimental data from Rejoub et al., Rapp and Englander-Golden, Tozer and Craggs, and Asundi and Kurepa.^{1–5} Discrepancies between calculated cross sections and experimental values suggest that a careful consideration of ionization efficiencies in an ion thruster is required.

B. Atomic propellants

Figure 1 describes the ionization cross sections for different atoms and shows different shapes with respect to threshold and absolute values, therefore, a comparison of these materials for the usage as propellants in an ion thruster has to be performed with the cross section and not only with the ionization threshold. A selection of atomic propellants with basic properties like atomic mass, ionization potential I_i and boiling temperature T_b is given in Table 1. With the information given there, it is obvious that an all-in-one propellant suitable for every purpose does not exist.

For instance, lithium has a low ionization potential and low cross section but needs high temperatures for evaporation; furthermore, the atomic mass is too low for a propellant. Cesium has the lowest ionization potential and the highest cross section for electron impact ionization, unfortunately, it is a very reactive material and has a low abundance on earth, therefore, it is one of the most expensive materials for electric

Table 1. Atomic mass M , Ionisation potential I_i and boiling temperature T_b for different elements suitable as a propellant for electric propulsion devices.

Element	M [u]	I_i [eV]	T_b [K]
Li	6.939	5.390	1603.0
Kr	83.800	13.996	121.1
Cd	112.400	8.991	1038.0
Sn	118.690	7.332	2893.0
I	126.900	10.440	457.2
Xe	131.300	12.127	165.2
Cs	132.905	3.893	963.2
Hg	200.590	10.434	630.2
Pb	207.190	7.415	2017.0
Bi	208.980	7.287	1833.0

propulsion (30,000 dollar per kg).⁶ Heavy materials like lead and bismuth need very high temperatures for evaporation, which is challenging from an engineering point of view in thruster design. In addition, metals have the disadvantage that they can form conductive layers on electric insulators, which lead to short circuits. Mercury has a high mass and a sufficient low boiling temperature, but is a high toxic material, which complicates its handling in a laboratory environment. Iodine has well-balanced material properties, but it is reactive and can cause problems when interacting with satellite surfaces like solar panels; furthermore, negatively charged ions can occur in the plasma, which reduces thrust efficiency.

The standard propellant for ionic electric propulsion is xenon, which offers a compromise: On one hand it has one of the highest ionization potentials compared to other materials, on the other hand it is a gaseous material under standard conditions and, therefore, less effort is required to transport the propellant from the storage vessel into the plasma chamber. In addition, it is a noble gas, hence, it will not interact with surfaces of the satellite, except through inevitable sputtering interactions. The price for xenon is relatively high, at present about 1300 Euro per kg, which is a strong increase if one compares this price with the given one of 850 dollar per kg by Kieckhafer and King in 2005.⁶ With this low price already both authors estimated the cost for a 500 kW Hall thruster running with 60% efficiency and 2000 s of Isp to be in the order of roughly 5000 dollar per hour.

C. Molecular Propellants

Molecular weights readily exceed the masses of the discussed atomic elements. Scharlemann discusses the feasibility of using Buckminsterfullerenes (C_{60}) as propellants.⁷ Leifer and Saunders hold a patent for using C_{60} as a propellant for electric propulsion.⁸ C_{60} is characterized by the highest stability of all fullerenes and has a molecular weight of 720.11 u. At room temperature it is a solid, that has to be evaporated by heating. Compared to xenon the higher mass results in a theoretical improvement of power saving of about 43%. However, it appears to be problematic that C_{60} decomposes above 800 °C, which is a natural limitation of vapor pressure. On the other hand, heating temperatures should be higher than 400 °C, otherwise resublimation occurs, which reduces thruster performance or clogs the propellant feeding line, hence, temperature control of the heating device has to be designed carefully. Anderson and Fitzgerald pointed out that fragmentation occurs also in inherent plasma processes, mainly after excitation via electron-impact ionization. Excited C_{60}^{+*} has an energy-dependent half life for fragmentation, usually in the order of μ s, and a residence time within the discharge vessel in the order of ms. Following Scharlemann the main problem of fullerenes, which excludes them as alternative propellants is due to a large cross section for negative ion formation, especially at low electron energies. Fullerene plasmas quench when only fullerenes are injected as carrier gas, hence, following his argument, a fullerene plasma can only be sustained with another support gas. Nevertheless, Anderson and Fitzgerald emphasized that few groups reported the successful operation of an ion thruster running with fullerenes.⁹ Another problem reported by them is the appearance of a black residual coating inside the plasma vessel, which may have negative effects regarding the lifetime of the thruster, for instance, due to a conductive coating of insulators.

Iodine has been already discussed in the previous section, nevertheless, its natural appearance is the iodine molecule I_2 . The dissociation energy of the iodine molecule I_2 is 1.54 eV, the ionization potential is 9.4 eV. The abundance of iodine in the Earth's crust is 25000 times higher than that of xenon, hence, the price for iodine is a factor 10 lower than for xenon. A big advantage is the solid appearance of iodine with a high density (4.94 g cm^{-3} , which is roughly three times higher than that for xenon, which reduces the storage volume considerably. On the other side the electron affinity of the molecule is 2.5 eV (for the atom it is 3.06 eV), which leads to the formation of negative charged species in the plasma. Nevertheless, iodine as a propellant has been investigated recently.^{6, 10–13}

D. Diamondoids

Diamondoids are an interesting group of materials with unusual chemical and physical properties that may make them attractive for electric propulsion. They are sp^3 -hybridized carbon clusters with the same structure as the cubic diamond lattice fully saturated with hydrogens. They are classified by the number of diamond cages n following the chemical formula $C_{4n+6}H_{4n+12}$.^{14, 15}

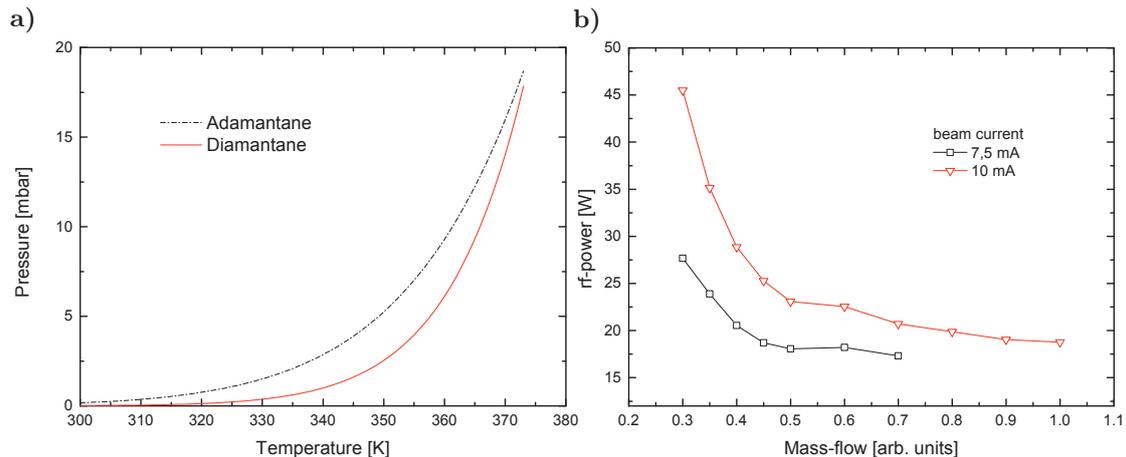


Figure 2. a) Saturated vapor pressure (in mbar) of adamantane and diamantane as a function of temperature (in Kelvin).²⁰ b) Performance mapping for adamantane using a radiofrequency ion source. A stable extraction of ions could be achieved for adamantane and the shape of the performance curves is in accord with the expected shape.

The smallest diamondoid, adamantane ($C_{10}H_{16}$), has an atomic mass of 136 u, which is slightly higher than that of xenon. The ionization potential of adamantane is 9.23 eV (diamantane: 8.8 eV, triamantane: 8.57 eV).¹⁶ Adamantane can be brought into the gas phase with very low heating power due to the sublimation of the material at fairly low temperatures. The vapor pressure as a function of temperature is shown in Fig. 2a. In a first experiment a radiofrequency-ion-thruster (RIT) was driven with adamantane to obtain a performance mapping (see Fig. 2b). Due to the lack of a calibration of the mass flow of adamantane the given mass flow is the equivalent of the xenon mass flow, therefore, a direct comparison of efficiencies is not possible. Nevertheless, we demonstrated that the plasma could be sustained with adamantane and that a stable extraction of ions could be achieved.

Like all molecular species diamondoids can decompose in plasma environments. In an ion thruster the ionization occurs through electron impact ionization, therefore, the interaction with electrons will contribute mainly to the fragmentation. To study the stability of diamondoids, mass spectrometry has been performed with adamantane, as described in section III. It should be mentioned that diamondoids have a negative electron affinity, hence, this can reduce propellant efficiency and should be considered carefully. An important aspect of diamondoids is the possibility to modify the molecular structure in a way as to optimize certain properties like the electronic structure.¹⁷⁻¹⁹ This could be exploited to reduce the ionization threshold or to increase the stability of the molecule in the plasma to suppress fragmentation. Upcoming activities at the Justus-Liebig-University will focus on this issue.

Another important aspect is the high abundance of diamondoids, in particular, of adamantane. They are a by-product of the petroleum industry. The percentage of adamantane in oil is in the order of 0.0004%, which makes them relatively cheap (prices vary between 1-100 dollar per kg).²¹

III. Mass spectrometry of diamondoids

A. Experimental setup

Mass spectrometry of adamantane has been performed at the Institute of Atomic and Molecular Physics. In first experiments a compact 10 GHz permanent-magnet electron-cyclotron-resonance-ion-source (ECRIS) was used to ionize the adamantane vapor, injected into the ion source from a reservoir by a needle valve.²² The reservoir was heated to increase the vapor pressure of the sublimated adamantane. The temperature was fixed at 60 °C. The needle valve was heated with a sleeve at 200 °C to avoid resublimation of adamantane inside the valve. The ion energy was adjusted at $q \times 6$ keV (with q denoting the ion charge). The mass analysis was accomplished with a double focussing dipole magnet with 90° bending angle which separates

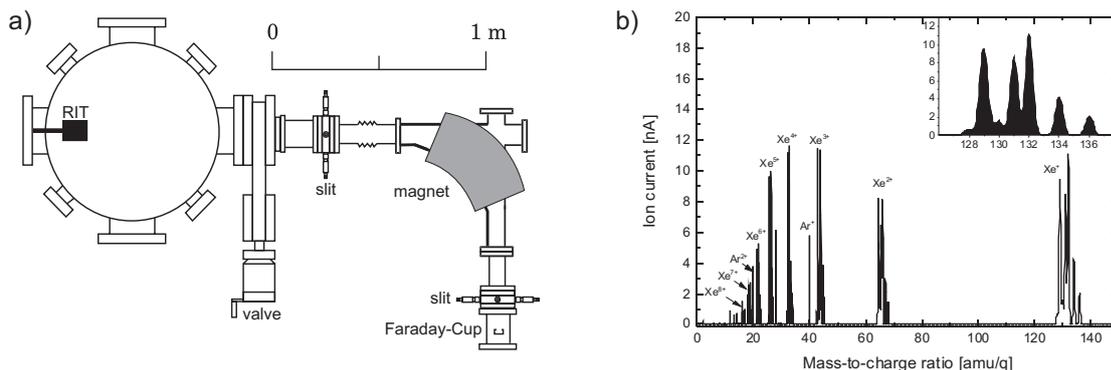


Figure 3. a) Experimental setup to perform mass spectrometry of ions extracted from a radiofrequency ion thruster. The incident ion beam is mass-to-charge analyzed by an 90° -deflection magnet. Ion currents are measured with a Faraday cup. b) Xenon mass spectrum of ions from an electron-cyclotron-resonance-ion-source (ECRIS) measured with the same kind of experimental apparatus. The ECRIS can easily produce high charge states of ions, therefore, it is an appropriate ion source to analyze fragmentation channels of a molecule. Nevertheless, the ECRIS will not facilitate a quantitative comparison of the fragmentation behavior of molecules with a RIT.

the incident ions according to their mass-over-charge ratio. The ion current behind the magnet was measured as a function of the magnetic field strength. A similar setup has been build at the Institute of Experimental Physics I for the analysis of the fragmentation of diamondoid molecules that occurs in a radiofrequency ion thruster (Fig. 3a). This setup is now in the commissioning phase and will be ready for experiments in the near future. A new gas-feed system to sustain the adamantane plasma is currently being assembled. Centerpiece of this device is a heatable mass-flow controller (MFC) calibrated for adamantane to measure performance mappings with this propellant. The MFC can be heated up to 150°C to avoid resublimation.

The ECRIS can easily produce high charge states of ions (see Fig. 3b). Therefore, it is an appropriate ion source to analyze fragmentation channels of a molecule but a comparison of the fragmentation behavior of molecules between ECRIS and RIT is not possible. The high efficiency of the ECRIS is due to the magnetic confinement of the plasma with a set of permanent magnets. Two dipole magnets achieve the axial confinement, a hexapole magnet the radial one. From the center of the plasma chamber the magnetic field is increasing in every direction. This minimum-B-structure increases the lifetime of the plasma, such that there is sufficient time for the electrons to gain adequate energy to ionize the injected gas to high charge states.

B. Results

Mass spectra of adamantane ionized in an ECRIS are shown in Fig. 4. The left spectrum was obtained with 25 W of rf power and a gas pressure of 5×10^{-5} mbar, while the right one was obtained with 20 W of rf power and a gas pressure of 3×10^{-4} mbar. Assuming that the gas pressure in a RIT-4 is in the order of a few 10^{-3} mbar, it is expected that the intensity of fragmentation will be significantly lower. Noticeable in both spectra is the very low intensity of H^+ and H_2^+ , which is unexpected regarding the fact that hydrogen is a component of the parent molecule. The split off hydrogen atoms do not contribute considerably to the mass spectra which can be explained with a low production rate as single molecule or with the high mean free path of this species reducing their confinement time in the plasma environment. Furthermore, the ionization cross section of hydrogen has a higher threshold than most of the other particles in the plasma and the maximum of the cross section is in the range of 50 Mb, which is relatively small compared to the presented cross sections in Fig. 1.

The general shape of the fragment distribution is in accordance with the published mass spectrum by Fort and Schleyer as well as by Waltman and Ling.^{21,23} The most favorable fragmentation channels are the loss of three and four carbon atoms. The mass $M/q = 26$ in Fig. 4a stands out in the spectrum at lower

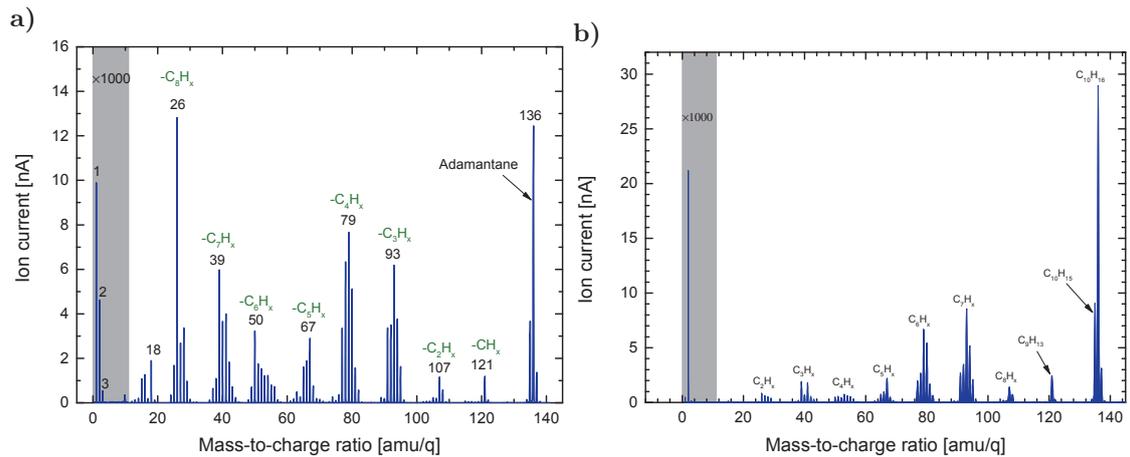


Figure 4. Mass spectra of adamantane obtained from an ECRIS with different source parameters to study the fragmentation behavior. The ECRIS-plasma is radially and axially confined by magnetic fields, therefore, higher charge states can be produced than in a RIT-plasma. Hence, the fragmentation of diamondoids in an ECRIS-plasma does not reflect the behavior of a RIT. However, it can give insight into the possible fragmentation channels. a) rf-power: 25 W, gas pressure: 5×10^{-5} mbar b) rf-power: 20 W, gas pressure: 3×10^{-4} mbar

mass-to-charge ratios and is probably due to multiple collision of heavier fragments with electrons leading to acetylene C_2H_2 as a favoured end product of the fragmentation channels.

IV. Conclusion

A comparison of various atomic and molecular materials being under discussion or used as propellants for ion thrusters has been presented. We point out that there does not exist a perfect material for this purpose, hence, for every ion thruster type pros and cons of the choice of the propellant need to be assessed and evaluated with respect to the requirements of the special mission. A new material has been proposed that may be suitable as an alternative propellant due to its basic properties and due to the possibility to modify the material by chemical methods in order to improve the desired properties. With the newly built mass spectrometer an analysis of pristine diamondoids and their functionalized derivatives will be performed in future experiments.

Acknowledgments

This work was supported in the framework of LOEWE-Schwerpunkt RITSAT by the Hessian State Ministry of Higher Education, Research and the Arts (HMWK). We also acknowledge financial support by Airbus DS.

References

- ¹Eugene J. McGuire. Electron ionization cross sections in the born approximation. *Phys. Rev. A*, 16:62–72, Jul 1977.
- ²R. Rejoub, B. G. Lindsay, and R. F. Stebbings. Determination of the absolute partial and total cross sections for electron-impact ionization of the rare gases. *Phys. Rev. A*, 65:042713, Apr 2002.
- ³D. Rapp and P. Englander-Golden. Total Cross Sections for Ionization and Attachment in Gases by Electron Impact. I. Positive Ionization. *The Journal of Chemical Physics*, 43(5):1464–1479, 1965.
- ⁴B. A. Tozer and J. D. Craggs. Cross Sections for Ionization of the Inert Gases by Electron Impact. *Journal of Electronics and Control*, 8(2):103–109, 1960.
- ⁵K. K Asundi and M. V. Kurepa. Ionization Cross Sections in He, Ne, Ar, Kr and Xe by Electron Impact. *Journal of Electronics and Control*, 15(1):41–50, 1963.
- ⁶A. Kieckhafer and L. B. King. Energetics of Propellant Options for High-Power Hall thrusters. In *Proceedings of the Space Nuclear Conference*, 2005.
- ⁷C. A. Scharlemann. Theoretical and experimental investigation of C_{60} -propellant for ion propulsion. *Acta Astronautica*, 51(12):865 – 872, 2002.

- ⁸S. D. Leifer and W. A. Saunders. Electric propulsion using C₆₀ molecules, August 31 1993. US Patent 5,239,820.
- ⁹J. R. Anderson and D. Fitzgerald. Fullerene Propellant Research for Electric Propulsion. In *AIAA-1996-3211*, 1996.
- ¹⁰J. Szabo, M. Robin, S. Paintal, B. Pote, V. Hrubby, and C. Freeman. Iodine Electric Space Propulsion. In *IEPC-2013 Proceedings 311*, 2013.
- ¹¹O.S. Tverdokhlebov and A. V.Semenkin. Iodine Propellant for Electric Propulsion To Be Or Not To Be. In *AIAA 2001-3350*, 2001.
- ¹²R. A. Dressler, D. J. Levandier, and Y. H. Chiu. Iodine electric propulsion thrusters, August 26 2003. US Patent 6,609,363.
- ¹³M. L. Hause, B. D. Prince, and R. J. Bernish. A guided-ion beam study of the collisions and reactions of I⁺ and I₂⁺ with I₂. *J. Chem. Phys.*, 142:074301, 2015.
- ¹⁴H. Schwertfeger, A. A. Fokin, and P. R. Schreiner. Diamonds are a Chemist’s Best Friend: Diamondoid Chemistry Beyond Adamantane. *Angew. Chemie Int. Edit.*, 47(6):1022–1036, 2008.
- ¹⁵J. E. Dahl, S. G. Liu, and R. M. K. Carlson. Isolation and structure of higher diamondoids, nanometer-sized diamond molecules. *Science*, 299(5603):96–99, 2003.
- ¹⁶K. Lenze, L. Landt, M. Hoener, H. Thomas, J. E. Dahl, S. G. Liu, R. M. K. Carlson, T. Möller, and C. Bostedt. Experimental determination of the ionization potentials of the first five members of the nanodiamond series. *J. Chem. Phys.*, 127:084320, 2007.
- ¹⁷T. Rander and M. Staiger and R. Richter and T. Zimmermann and L. Landt and D. Wolter and J. E. Dahl and R. M. K. Carlson and B. A. Tkachenko and N.A. Fokina and P. R. Schreiner and T. Möller and C. Bostedt. Electronic structure tuning of diamondoids through functionalization. *The Journal of Chemical Physics*, 138(2):-, 2013.
- ¹⁸B. Adhikari and M. Fyta. Towards double-functionalized small diamondoids: selective electronic band-gap tuning. *Nanotechnology*, 26:035701, 2014.
- ¹⁹M. A. Gunawan, J.-C. Hierso, D. Poinot, A. A. Fokin, N. A. Fokina, B. A. Tkachenko, and P. R. Schreiner. Diamondoids: functionalization and subsequent applications of perfectly defined molecular cage hydrocarbons. *New J. Chem.*, 38:28–41, 2014.
- ²⁰M. A. Gunawan, D. Poinot, B. Domenichini, C. Dirand, S. Chevalier, A. A. Fokin, P. R. Schreiner, and J.-C. Hierso. The functionalization of nanodiamonds (diamondoids) as a key parameter of their easily controlled self-assembly in micro- and nanocrystals from the vapor phase. *Nanoscale*, 7:1956–1962, 2015.
- ²¹Raymond C. Fort and Paul von R. Schleyer. Adamantane: Consequences of the diamondoid structure. *Chemical Reviews*, 64(3):277–300, 1964.
- ²²M. Liehr and M. Schlapp and R. Trassl and G. Hofmann and M. Stenke and R. Völpel and E. Salzborn. Investigations of the new giessen 10 {GHz} electron-cyclotron-resonance ion source. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 79(14):697 – 700, 1993.
- ²³R. J. Waltman and A. Campell Ling. Mass spectrometry of diamantane and some adamantane derivatives. *Can. J. Chem.*, 58:2189–2195, 1980.